Supporting Information for

CdSe Quantum Dot (QD) and Molecular Dye-Hybrid Sensitizers for TiO_2 Mesoporous Solar Cells: Working Together with a Common Hole Carrier of Cobalt Complexes

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1) Experimental details

CdSe QD preparation by SILAR process: The optimized FTO/TiO_2 film was successively immersed for 30 seconds, inside a glove bag under inert atmosphere first in 0.030 M $Cd(NO_3)_2$ followed by in 0.030 M selenide both in ethanol. Following each immersion, the films were rinsed for 1 min or longer with pure ethanol to remove excess precursors and dried before the next dipping. This immersion cycle was repeated five times for growing CdSe QD, followed by a passivation layer of CdTe. Selenide (Se^{2-}) was prepared *in-situ* by adding 0.0680 g of $NaBH_4$ (to make up 0.060 M) to 0.030 M SeO_2 in 30 ml ethanol while the round bottom flask-container was purged by Ar or N_2 and telluride was prepared in a similar way as reported recently.[1]

Cell fabrication and measurement: Photoelectrodes consisted of a TiO_2 film with a triple layer structure were prepared by following the optimal condition reported for cobalt complex-based redox couples.[2] A compact blocking underlayer of spray-pyrolyzed titanium dioxide (ca. 100 nm thick) was deposited onto a cleaned conducting

glass substrate (NSG, F-doped SnO_2, resistance 8 Ωsq^{-1}). A solution of titanium diisopropoxide bis(acetylacetonate) in ethanol was sprayed 16 times over the conducting glass surface, which was maintained at 450 ^oC. The treated glass plates were fired at 450 ^oC for 30 min. more to remove remaining organic traces. Successive depositions of about 2.1 μm thick transparent layer from 20 nm-TiO_2 and about 6.2 μm thick 60 nm-TiO_2 (gift from Showa Titanium company) light-scattering layer by screen-printing, and final post-treatment with an aqueous solution of $TiCl_4$ were then carried out according to typical procedures done in our laboratory for dye cells.[3]

After CdSe QD's derivatization of nanocrystalline oxide films was obtained by following the typical SILAR process described above, the QD-sensitized photoanodes were immersed into two different dye solutions for 4 hours; 1) 0.3 mM Z907Na in acetonitrile/*tert*-butanol (1:1) and 2) 0.1 mM SQ1 in ethanol. Then, the QD- or QD/dye hybrid-sensitized electrodes were assembled and sealed with a thin transparent hot-melt 25 μm thick Surlyn ring (DuPont) to the counter electrodes (Pt on FTO glass, chemical deposition of 0.05 M hexachloroplatinic acid in 2-propanol at 400 ℃ for 20 min). The electrolyte was injected into the interelectrode space from the counter electrode side through a predrilled hole, and then the hole was sealed with a Bynel sheet and a thin glass slide cover by heating. All the procedures in preparing electrodes and assembling those were the same as in our typical dye-sensitized cells,[3] except one step of QDs attachment over TiO_2 layers.

The irradiation source for the photocurrent-voltage (*I-V*) measurement is a 450 W xenon light source (Osram XBO 450, USA), which simulates the solar light. The incident light intensity was calibrated with a standard Si solar cell. The spectral output of the lamp matched precisely the standard global AM 1.5 solar spectrum in the region

of 350-750 nm (mismatch < 2%) by the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany). Various irradiance intensities from 0.01 to 1.0 sun can be provided with neutral wire mesh attenuators. The current-voltage curves were obtained by measuring the photocurrent of the cells using a Keithley model 2400 digital source meter under an applied external potential scan. The measurement of incident photon-to-current conversion efficiency (IPCE) was performed by a similar data collecting system but under monochromatic light. IPCE was plotted as a function of excitation wavelength. The incident light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the cell under test.

Preparation of four different electrolytes:

1) Iodide/triiodide-based one: an 1.0 M of 1, 3-dimethylimidazolium iodide, 50 mM of LiI, 0.50 M of *t*-butylpyridine, 30 mM of I_2, and 0.10 M GuSCN dissolved in a mixture of acetonitrile and valeonitrile (85:15/v:v).
2) Polysulfide-based one: a 0.60 M of Na_2S, 0.20 M S, and 0.20 M KCl dissolved in a mixture of H_2O and methanol (7:3/v:v).
3) Disulfide/thiolate (T_2/T^-, where T^- represents the 5-mercapto-1-methyltetrazole ion and T_2 stands for its dimer)-based one[4]: a 0.40 M of T_2, 0.40 M of T^-, 0.50 M of *t*-butylpyridine, and 50 mM of $LiClO_4$ dissolved in a mixture of acetonitrile and ethylene carbonate (6:4/v:v).
4) Cobalt complex-based one[1]: a 0.75 M $Co(o\text{-}phen)_3^{2+}$, 0.075 M $Co(o\text{-}phen)_3^{3+}$, and 0.20 M $LiClO_4$ dissolved in acetonitrile/ethylene carbonate (4:6/v:v).

The cobalt (II/III) complex, $[Co(o\text{-}phen)_3](TFSI)_{2/3}$, (o-phen=1,10-phenanthroline and TFSI = bis(trifluoromethanesulfonyl)imide) was synthesized according to literature procedures,[5] which was briefly described as like below;

A solution of $CoCl_2$ (0.25 g, 1.05 mmol) in water is added drop wise to a methanolic solution of (3.15 mmol) ligand (o-phen), and the solution turns yellow immediately. To this solution add LiTFSI (0.80 g) in 10 ml water and immediately got the precipitate. Filter the complex and washed with water and dried under vacuum to get $Co(o\text{-}pen)_3(TFSI)_2$.

A solution of $CoCl_2$ (0.25 g, 1.05 mmol) in water is added drop wise to a methanolic solution of (3.15 mmol) ligand (o-phen), and the solution turns yellow immediately. To this solution add a methanolic bromine solution and immediately get some precipitate. Separate the precipitate and to the filtrate add LiTFSI (1.20 g) dissolved in 15 ml of water to get the precipitate of oxidized form of the cobalt complex. Collect the precipitate and wash with water and dried under vacuum to isolate $Co(o\text{-}phen)_3(TFSI)_3$.

References

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2) TEM images

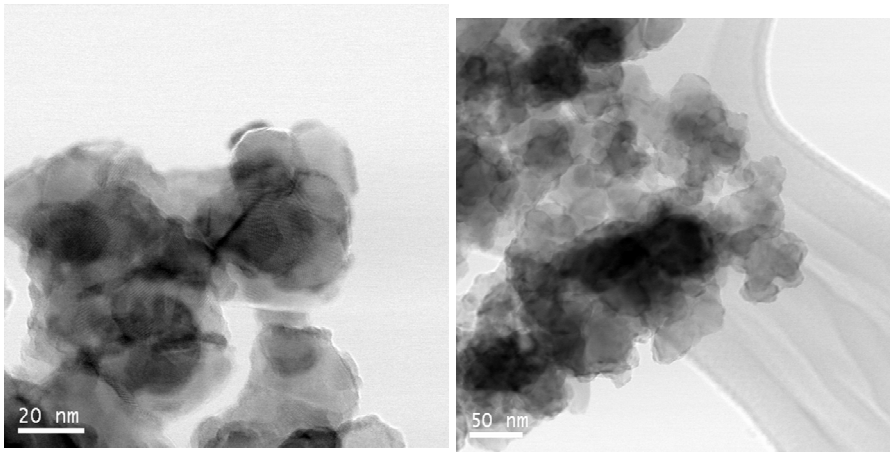

Figure S1. High resolution TEM images of CdSe QDs deposited onto the TiO_2 particles (20~30 nm) connected. A few nanometer-sized smaller particles (CdSe QD) were seen to be scattered upon the surface of larger TiO_2.

3) Dyes

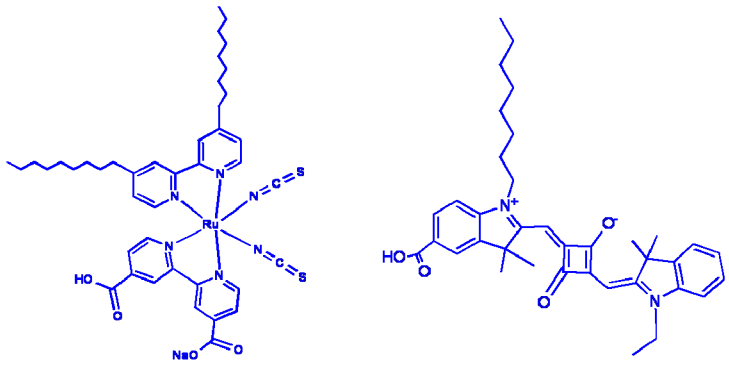

Figure S2. Molecular structures of dyes used for making hybrid sensitizers.